Study on the specific heat of wood by statistical mechanics

YANG Qing-xian (杨庆贤)

(Department of Basic Science, Fujian Forestry College, Nanping 353001, P. R. China)

Abstract: From the microstructure of wood, theoretical expressions of the wood specific heat were derived by statistical mechanics. With the theoretical expressions derived, the theoretical values of specific heat for 33 tree species, with different moisture contents and under varied temperature conditions were calculated and comparison was also made to the experimental values under the same conditions. The results showed that the maximum error and mean error by the theoretical expressions of this paper are only 7.8% and 2.5% respectively, while those error of the theoretical values for 33 tree species calculated with Dunlap's empiric equation were 15.2% (max.) and 9.3% (mean), and for Кириллов empiric equation, they were 20% (max.) and 11% (mean).

Keywords: Specific heat; Wood; Theoretical expression

CLC number: S781.37   **Document code:** A   **Article ID:** 1007-662X(2000)04-0265-04

Introduction

Since wood is a natural macromolecular organism, and chemical composition, structure and biological cell structure of wood are extremely complicated, these cause great difficulty to the theoretical study on the specific heat of wood. So far, any research achievement has not been reported on it.

We try theoretically to find out the internal relation and essential laws between the specific heat of wood and the microstructure of wood, reveal the internal factors and the external conditions of affecting the specific heat of wood, and finally derive a theoretical expression of specific heat of wood, it can be used to replace the experimental which measurement of the wood specific heat.

Microstructure of wood

The physical property of wood depends mainly on substances composing the cell wall of wood, and cellulose is the major composition of the cell wall. Proved by X-ray diffraction, all natural cellulose have the same X-ray diffraction pattern, which indicates that all natural celluloses have the same crystal structure. The smallest unit of the crystal structure of cellulose is cell. The model of unit cell belongs to the monoclinic system, and the length of axis is a=0.835 nm, b=1.03 nm, c=0.79 nm respectively and the angle β between a axis and c axis is 84°. There are four glucose radicals ($C_6H_{10}O_5$) in each cell, and the

volume of each glucose radical is

$$v = \frac{1}{4} abc\sin\beta = 0.1689 \times 10^{-27} m^3.$$

Theoretical expression of specific heat of wood

First let's consider such a molecular crystal which contains N molecules and each molecule is composed of S atoms. It is assumed that there are $3N$ modes of vibration whose frequency distribution can be approximated according to Debye's theory and the frequency distribution of the other $3N(S-1)$ modes of vibration can be approximated according to Einstein's theory. Then the logarithm of the crystal partition function $K(T)$ can be expressed as

$$\ln K(T) = \left[\prod_{i=1}^{N} \frac{\exp(-h v_i / 2kT)}{1 - \exp(-h v_i / 2kT)}\right] +$$
$$N \ln\left[\prod_{i=4}^{3s} \frac{\exp(-h v_i / 2kT)}{1 - \exp(-h v_i / 2kT)}\right] =$$
$$-\frac{E_0}{kT} - \frac{9N}{v_r^3}\int_0^{v_r} v^2 \ln(1 - \exp(-hv/kT))dv -$$
$$N\sum_{i=4}^{3s} \ln(1 - \exp(-h v_i / kT)) \qquad (1)$$

Where E_0 is zero point vibrational energy of the crystal. From expression (1) we can get the heat capacity of the molecular crystal at constant volume.

$$C_V = \frac{k}{T^2}\left[\frac{\partial^2 \ln K(T)}{\partial(\frac{1}{T})^2}\right]_{V,N} = 3NkD\left(\frac{\Theta_D}{T}\right) +$$
$$Nk\sum_{i=4}^{3s} \frac{(\Theta_i/T)^2 \exp(\Theta_i/T)}{[\exp(\Theta_i/T)-1]^2} \qquad (2)$$

Where $\Theta_i = \frac{h\nu_i}{k} \cdot \Theta_D \cdot D(\frac{\Theta_D}{T})$ are respectively called Debye characteristic temperature and Debye function. Their expressions are respectively

$$\Theta_D = \frac{h\nu_D}{k} = \frac{hu}{k}\left(\frac{3}{4\pi v}\right)^{1/3} \tag{3}$$

$$D\left(\frac{\Theta_D}{T}\right) = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx \tag{4}$$

Where u is sound velocity of wood, v is each molecules' volume and $x = \frac{h\nu}{kT}$.

But the problem is that the celluloses can't be simply regarded as the crystal composed of the molecules, for every glucose radical doesn't lie in the similar place of the lattice. On the average, every four glucose radicals forms a cell which repeats itself, namely the cellulose belongs to the complicated lattice crystal. So we can't make direct use of expression (2) to calculate the specific heat of wood.

In Born's view (Qian 1962), a crystal containing N cells with SN atoms can have 3s groups of different normal modes of vibrations and frequencies. The wave numbers of each group is uniform distribution in the three-dimensional space. To every wave number, there is correspond to two frequencies, a higher frequency which hardly depends on the wave number to remain a constant is called optical mode

of vibration, a lower frequency which almost keeps direct proportional to wave number is called acoustical mode of vibration. In the crystal made up of N single cells, each group composed of N acoustical modes of vibration contributes a Debye term, while each group composed of N optical modes of vibration contributes an Einstein term. So any crystal partition function can roughly be expressed with the product of 3S partition functions. Suppose in 3S partition functions there is 3a belong to the Debye type (Here a is equal to one at least) and all the other $3(s-a)$ belongs to the Einstein type. For this reason expression (2) can be changed into

$$C_v = 3aNkD(\frac{\Theta_D}{T}) + Nk\sum_{i=3a+1}^{3s} \frac{(\Theta_i/2T)^2}{\sinh^2(\Theta_i/2T)} \tag{5}$$

The determination of how many groups of vibration modes in the 3S groups belong to the acoustical mode and how many groups belong to the optical mode depends on the particular structure of the crystal. As far as the cellulose crystal of wood is concerned, it is linear macromolecule. The basic unit of the cellulose structure is D-glucose. The cellulose is a chain-shaped molecule joined by β -1, 4-glucosidic linkages without any branches. The chemical structure of the big cellulose molecule is represented in Fig. 1.
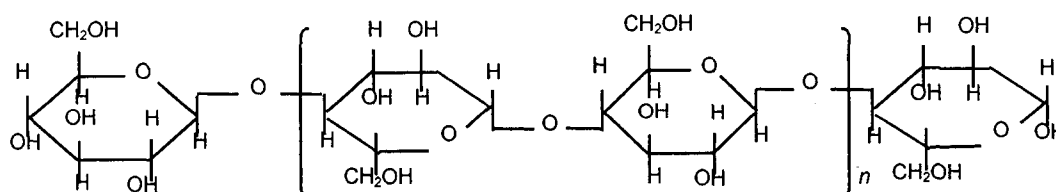

Fig. 1 Chemical structure of the cellulose

The cellulose molecule in the long chain direction combines to form a succession structure depending on valence bonds, and in side direction it forms associated molecular bundle depending on hydrogen bonds. It is the parallel arrangement of the molecular chain with excellent direction and the associated hydrogen bonds in the side direction that form crystal structure of wood cellulose.

According to the above wood cellulose's chemical constitution and crystal structure, we can put forward the microstructure model of cellulose crystal to derive specific heat of wood, as shown in Fig.2. It is clear that a pyran-ring is made up of 20 atoms, 60 degrees of freedom, 54 degree of freedom of internal vibration, including the stretching and bending vibration of

C—C, C—H, C—O, O—H bonds. They all belong to the optical mode of vibration, and each contributes an Einstein term. As to the other 6 freedom degrees, one half are translation degree of freedom in the mass center of pyran-ring, the other are rotary degree of freedom. Because the pyran-ring is a looped structure as and too large to be considered as a particle, we have to consider its rotary motion. These 6 degrees of freedom satisfy the dispersion relation of acoustical motion and each contributes a Debye term. As to the oxygen atoms between the pyran-rings, the intensity of C—O bond is similar to that inside the pyran-ring, but the bonds on the pyran-ring form a cyclic construction which can be considered as a whole unit. At the same time, the mass of the oxygen

atom between the two pyran-rings is much smaller than the total mass of the atoms in the pyran-ring. Therefore, it can't form Debye term.
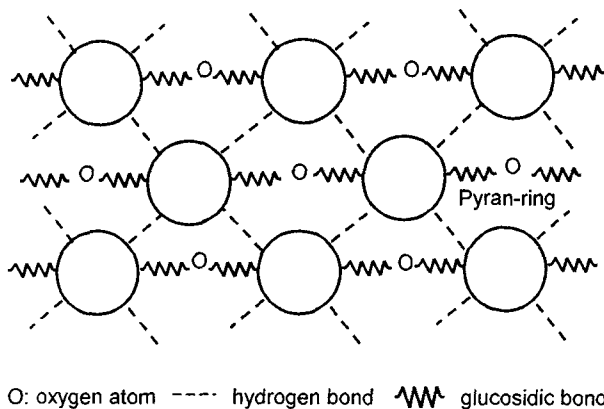

O: oxygen atom ---- hydrogen bond ⋀⋀⋀ glucosidic bond

Fig. 2 The model of cellulose structure for theoretically deriving wood specific heat

So these 3 freedom degrees of the oxygen atom between the two pyran-rings belong to the optical mode of vibration and each contributes an Einstein term too. Thus, equation (5) can be turn into

$$C_v = 6RD(\frac{\Theta_D}{T}) + R\sum_{v=1}^{57}\frac{(\Theta_v/2T)^2}{\sinh^2(\Theta_v/2T)} \qquad (6)$$

In this way we can obtain the theoretical expression of dry wood specific heat.

$$C_0 = \frac{R}{\mu}\left[6D(\frac{\Theta_D}{T}) + \sum_{v=1}^{57}\frac{(\Theta_v/2T)^2}{\sinh^2(\Theta_v/2T)}\right] \qquad (7)$$

Where R is universal constant of gases, μ is molar mass of a glucose radical, and Θ_v is the characteristic temperature of each chemical bond in a pyran-ring.

In order to simplify calculation, we can expand expression (7) into Taylor series at $T=T_0(T_0=273.15$ K). When the series is kept to the first order of solution, we obtain

$$C_0(t) = \frac{R}{\mu}\left[6D(\frac{\Theta_D}{T_0}) + \sum_{v=1}^{57}\varepsilon(\frac{\Theta_v}{T_0})\right] +$$

$$\frac{2R}{\mu T_0}\left\{9\left[D(\frac{\Theta_D}{T_0}) - \varepsilon(\frac{\Theta_D}{T_0})\right] + \sum_{v=1}^{57}\varepsilon(\frac{\Theta_D}{T_0})\left[Ch\left(\frac{\Theta_v}{2T_0}\right)\sqrt{\varepsilon(\frac{\Theta_v}{T_0})} - 1\right]\right\}t \qquad (8)$$

where $\varepsilon\left(\frac{\Theta_v}{T}\right) = \left[\frac{\Theta_v}{2T}/\sinh\left(\frac{\Theta_v}{2T}\right)\right]^2$ is Einstein's function. Substituting known quantity into Eq.(8), we still further obtain more simply theoretical expression of the wood specific heat

$$C_0(t) = 1.2294 + 0.006714t \qquad (kJ \cdot kg^{-1} \cdot K^{-1}) \qquad (9)$$

The relationship between the specific heat of the wet wood C_w (whose moisture content is w%) and that of the absolutely dry wood C_0 (it is expressed in Equation (9)) is given by the equation

$$C_w = \frac{C_0 + C'W\%}{1 + W\%} \qquad (10)$$

Comparison between the theoretical value and experimental value

We calculated the specific heat of 33 species of trees with different moisture contents and temperature by means of equations (9) and (10), and made a comparison between the theoretical values of specific heat and their experimental values under the same condition (temperature and moisture content). The results are shown in Table 1.

Conclusion

The comparison between the theoretical values and the experimental ones of the specific heat in the 33 species of wood with different moisture contents and temperature in Table 1 shows that the maximum error is 7.8%, and the average error is 2.5%.
If the specific heat of the 33 species of wood in Table 1 is calculated by Dunlap's (Cheng et al. 1985) empiric equation

$$C_0 = 0.266 + 0.00116t \qquad (cal \cdot g^{-1} K \cdot ^1)$$

Or by Кириллов empiric equation

$$C_0 = 0.28\left(1 + \frac{t}{100}\right)^{0.2} + 0.09 \qquad (cal \cdot g^{-1} K \cdot ^1)$$

it can be found that the maximum error of the former is 15.2% and that of the latter 20%, and the average error of the former is 9.3% and that of the latter 11%.
As shown above, theoretical expression of wood specific heat that is derived using statistical thermodynamics from the microstructure of wood is a more accurate formula.

Table 1. Theoretical and experimental values of specific heat in 33 species of wood

Species of trees	Moisture content /%	Temperature /°C	Specific heat /kJ · kg⁻¹ · K⁻¹		Error /%
			Theoretical	Experimental.	
Picea jezoensis var. komarovii	12.7	16.5	1.661	1.624	+2.3
Pinus koraiensis	11.0	16.5	1.623	1.666	- 2.6
Cunninghamia lanceolata	17.0	23.5	1.794	1.762	+1.8
Pinus massoniana	14.6	24.2	1.748	1.737	+0.5
Podiocarpus imbricatus	13.6	17.4	1.687	1.687	0
Larix olgensis	14.5	13.9	1.686	1.720	- 2.0
Paulownia fargesii	10.5	17.2	1.615	1.670	- 3.3
P. fortunei	13.0	21.7	1.699	1.725	- 1.5
P. elongatei	12.4	22.6	1.691	1.754	- 3.6
P. austrais	12.9	21.2	1.693	1.649	+2.7
P. kawakamii	11.0	18.7	1.636	1.649	- 0.8
P. catalpifolia	12.7	22.4	1.696	1.770	- 4.2
P. tomentosa var. tsinlingensis	11.3	17.6	1.636	1.695	- 3.5
P. tomentosa	13.0	22.4	1.703	1.712	- 0.5
Populus euramericana	12.1	18.3	1.658	1.633	+1.5
Gossampinus malabaricus	15.1	23.7	1.755	1.628	+7.8
Alniphyllum fortunei	13.9	24.5	1.734	1.725	+0.5
Tilia mandshurica	10.9	16.0	1.617	1.615	+0.1
Juglans mandshurica	14.5	16.1	1.699	1.720	-1.2
Catalpa duolouxii	17.3	26.0	1.814	1.875	-3.2
Populus simonii	13.3	15.8	1.671	1.636	+2.1
Melia azedarach	15.3	24.5	1.764	1.720	+2.6
Manglietia hainanenss	12.7	21.0	1.688	1.712	-1.4
Ulmus sp.	10.1	25.0	1.653	1.670	- 1.0
Betula platyphylla	13.2	16.7	1.674	1.633	+ 2.5
Acer davidii	12.3	24.5	1.699	1.716	- 1.0
Acer mono	11.7	25.0	1.689	1.712	-1.3
B. alnoides	15.3	24.2	1.762	1.746	+0.9
Fraxinus mandshurica	12.1	26.0	1.704	1.771	-3.8
Quereus mongolica	12.7	25.0	1.711	1.846	-7.3
Schima wallichii	16.0	23.6	1.774	1.725	+2.8
Homalium hainanense	12.0	24.0	1.690	1.771	-4.6
Quercus acutissima	14.8	21.0	1.733	1.880	-7.8

Acknowledgements

References

Cheng Junqun, *et al.* 1985. Wood science [M]. Beijing: China Forestry Publishing House, p490.

Qian Xuesen. 1962. Teaching Materials of physical mechanics [M]. Beijing: Science Publishing house, p156-162.